IDENTIFYING THE CONTRIBUTING SOURCES OF PCDDs/PCDFs BY COMPARISON OF CONGENER DISTRIBUTION PROFILES OBSERVED IN RESPIRABLE SUSPENDED PARTICULATE MATTER SAMPLED FROM AMBIENT AIR OF DELHI

Kumar Sanjay[1], Lal R.B.[1], Kumar. B.[1], Sharma C.S.[1], Makhijani S.D.[1], Kamyotra J. S.[1], Gautam S.P.[1]

[1]National Reference Trace Organics Laboratory, Central Pollution Control Board, Delhi - 110032, INDIA

Abstract

PCDDs/PCDFs (17 congeners) are regularly being monitored in the respirable suspended particulate matter from ambient air at several locations of Delhi, consequently significant amount of data has been generated. This baseline data has been used for identification of emission sources releasing these compounds into ambient air by comparing the average congener profiles (percent ratio of individual concentration of 2,3,7,8 substituted congeners to the total concentration of 2,3,7,8 substituted congeners) from each location with congener profiles for various specific emission sources available in literature. It is observed from the comparison of congener profiles from each location with source specific congener profiles that the impact of thermal power plants and medical / hospital waste incinerator is dominant on surrounding locations nearby these sources respectively. The locations farther from these major sources are found to have impact of local industrial units burning various fuels and probably mixed industrial wastes, however, the contribution of automobiles sources can be attributed to all locations in metropolitan city Delhi. For conclusive identification of various sources of PCDDs/PCDFs, further studies would be undertaken for establishing source specific congener profiles, including more locations as possible receptors for specific source categories and including congeners other than 2,3,7,8-substituted congeners.

Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are two groups of halogenated organic compounds with similar properties[1]. A large number of different combinations of both the number of chlorine atoms and position of substitution is possible. As a result there are 75 different PCDD and 135 PCDF, or altogether 210 different compounds[2]. However, only the isomers with chlorine substituted in the 2,3,7,8 positions have been reported to be toxic to exposed organisms. This reduces the number of compounds of interest to 17 (7 PCDDs and 10 PCDFs)[1]. PCDDs and PCDFs are mainly the by-products of industrial processes such as metallurgical processing, bleaching of paper pulp, and the manufacturing of some herbicides and pesticides[1]. Waste incineration, particularly if combustion is incomplete, is among the largest contributors to the release of PCDDs and PCDFs into the environment[1].

In the present study the respirable suspended particulate matter samples collected from ambient air at several locations within national ambient air monitoring programme network have been used for assessment of 17 congeners of PCDDs/PCDFs (chlorine substituted at positions 2,3,7,8). The data generated has been used for identification of emission sources releasing these compounds into ambient air by comparing the average congener profiles (percent ratio of individual concentration of 2,3,7,8 substituted congeners to the total concentration of 2,3,7,8 substituted congeners) from each location with those reported in literature for various specific emission sources.

In Delhi metropolitan city, there are three major coal based thermal power plants, one gas based power plant and a few hospital waste incinerators. Though there exists no organized municipal waste incineration but the municipal waste is sometimes burnt near inhabited localities in small quantities, however, major portion of municipal waste is transported to sanitary landfills for disposal. The vehicle count in Delhi is alarmingly high at more than 5 million vehicles (cumulative total of various types of combustion engine vehicles). Unleaded petrol had been introduced in the city a decade back and majority of private four wheel and two wheel vehicles are operated with on unleaded petrol, the state owned public transport buses, private owned public transport buses and privately owned three wheelers run on compressed natural gas (CNG), approx 20% four wheel vehicles run on compressed natural gas (CNG) as well as liquefied petroleum gas (LPG), the commercial goods transport vehicles are mostly diesel driven. Diesel is also being used for back up electric generation in small scale industries, construction sites and larger offices.

Materials and Methods

Internationally practiced methods e.g. German Guideline VDI 3498 Part-1, European Standard EN 1948 and USEPA Methods 8290 and 23 are referred for analytical procedures. Solvents, reagents and standard reference solutions (calibration solutions CS1 to CS5, extraction spike solution and syringe spike solution as per EN 1948) had been procured from Merck, Sigma-Aldrich and Wellington Laboratories Inc. / Cambridge Isotopes Ltd. respectively.

The monitoring locations of NAAMP (National Ambient Air Monitoring Programme) of Delhi, had been used for Ambient Air Sampling in this study, may be described below based on the prevailing emission sources prevailing near these locations. Station CE is located at central east Delhi near one of the most busy traffic intersections and thermal power plants in the vicinity. The station S is located at southern part of Delhi and relatively farther from power plants but nearer to medical waste incinerator. The station W is located at western part of the city farther from larger stationary sources but near to congregation of small scale industries. The station N is located at northern part of the city and there are no major specific sources near to this location except some small scale industries. The station NE is located at north eastern periphery of the city and some small scale industries using variety of fuel options are characteristic in this region, in addition there are few scrap iron recycling units in nearby areas.

Samples had been collected on `Whatman' glass fiber filter papers (GF/A) by respirable suspended particulate matter sampler (modified high volume sampler with cyclone for particle size cut off) operated for three eight hourly shifts. At least two 24 hourly samples had been taken (three eight hourly samples combined) in each month for all identified monitoring locations.

Samples had been extracted by Soxhlet apparatus, subjected to acid-silica, multi-layered silica and alumina column chromatography sequentially for destruction of aliphatic hydrocarbons, removal of sulfur compounds and other co-extracted interfering compounds and separation of dioxin furan from PCBs respectively. Isotope labeled internal standards had been used for quality control by calculation of recovery rates for extraction and cleanup, and quantification of target PCDDs/PCDFs congeners.

Concentrated sample extracts have been analysed by JEOL JMS 800D GC-HRMS with DB-Dioxin column for separation of individual congeners, SIM mode of data acquisition at resolution >10000 and positive electron ionization. The instrument was calibrated by initial five level calibrations and subsequent daily verification by any one of those levels. In case of deviation outside permitted quality control limits the fresh multi-level calibration was performed. The chromatograms of two mass fragments of target congeners and two mass fragments of isotope labeled congeners have been manually evaluated for quality assurance.

Results and Discussion

The congener profiles specific to various source emissions have been discussed in several studies[3,4,5,6]. The generalizations detailed in USEPA report[3], which are relevant to the identified stationary sources and automobiles in locations of this study are as follows.

- The combustion sources emit all 2,3,7,8 substituted CDDs and CDFs, although in varying percentages of total CDD/CDF. OCDD dominates total emissions from industrial oil-fired boilers; from unleaded gasoline combustion; and from diesel fuel combustion in vehicles.

- The dominant congeners in emissions from for other combustion sources are: OCDF in emissions from medical waste incineration; 1,2,3,4,6,7,8-HpCDF from hazardous waste incinerators; 2,3,4,7,8-PeCDF from cement kilns burning hazardous waste; 2,3,7,8-TCDF from cement kilns not burning hazardous waste; OCDF in industrial/utility coal-fired boilers.

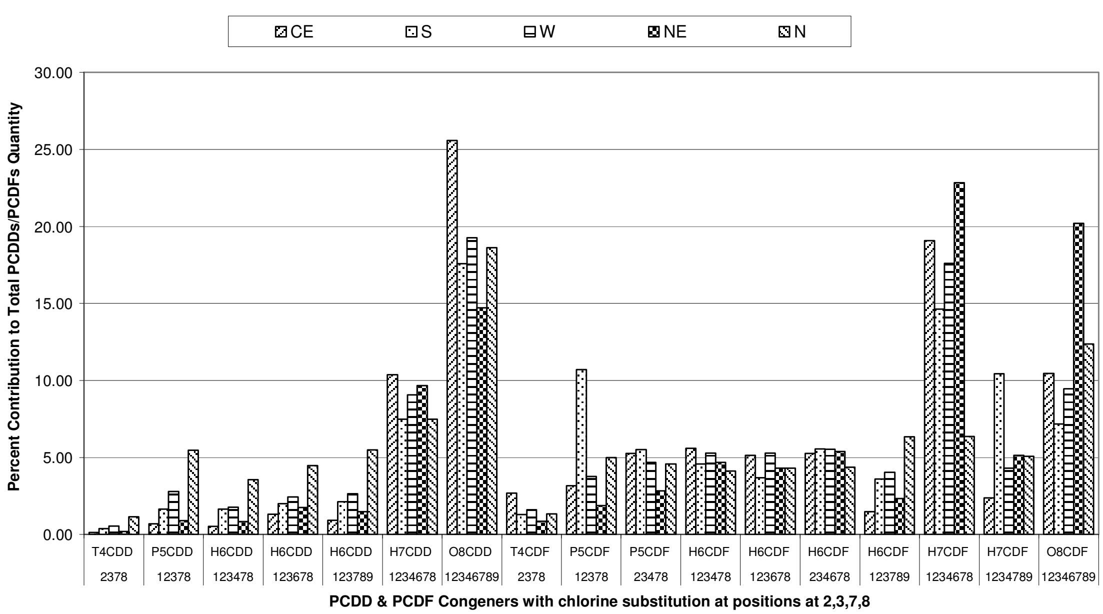
- There are similarities in the congener profiles of diesel driven vehicle emissions, unleaded gasoline vehicle emissions, and industrial wood combustors. In these sources, OCDD dominates total emissions, but the relative ratio of 1,2,3,4,6,7,8-HpCDD to OCDD is also quite similar.

The measured concentrations of 17 congeners (2,3,7,8-substituted) of PCDDs/PCDFs of this study have been compiled, outliers have been left out, and remaining good quality data have been converted to congener profiles (percent distribution ratios) by dividing concentration of individual congener by total concentration of 17 congeners. The congener profiles for five locations have been compiled and presented in Table 1.

Table 1: Congener Profile of PCDDs/PCDFs in RSPM of Ambient Air of Delhi

		Locations					
Isomer	**Compound**	**CE**	**S**	**W**	**NE**	**N**	**Avg.**
2378	T4CDD	0.12	0.39	0.54	0.18	1.14	0.47
12378	P5CDD	0.70	1.64	2.77	0.90	5.46	2.29
123478	H6CDD	0.53	1.65	1.77	0.84	3.55	1.67
123678	H6CDD	1.31	1.99	2.44	1.75	4.47	2.39
123789	H6CDD	0.91	2.12	2.64	1.49	5.49	2.53
1234678	H7CDD	10.38	7.48	9.07	9.66	7.48	8.81
12346789	O8CDD	25.59	17.58	19.26	14.73	18.61	19.16
2378	T4CDF	2.68	1.30	1.60	0.86	1.33	1.55
12378	P5CDF	3.16	10.72	3.76	1.86	5.00	4.90
23478	P5CDF	5.26	5.51	4.68	2.83	4.58	4.57
123478	H6CDF	5.59	4.56	5.28	4.68	4.11	4.85
123678	H6CDF	5.12	3.67	5.28	4.31	4.30	4.54
234678	H6CDF	5.26	5.56	5.52	5.37	4.37	5.22
123789	H6CDF	1.48	3.61	4.03	2.34	6.33	3.56
1234678	H7CDF	19.09	14.65	17.61	22.84	6.36	16.11
1234789	H7CDF	2.38	10.42	4.30	5.14	5.06	5.46
12346789	O8CDF	10.45	7.16	9.46	20.20	12.36	11.93
Total PCDDs/PCDFs		100.00	100.00	100.00	100.00	100.00	100.00

Figure 1 : Congener Distribution Profile in RSPM of Ambient Air of Delhi



On the basis of observations and comparison of average PCDDs/PCDFs congener profiles for each monitored locations during the study, the following inferences can be made;

- At location CE, the congener profile reflects a combined effect of coal fired power generating facilities (higher contribution of 1,2,3,4,6,7,8 HpCDD and OCDD compared to rest of dioxin congeners), automobiles run on leaded petrol (higher contribution of 1,2,3,4,6,7,8 HpCDF) & unleaded petrol (higher contribution of OCDD) and medical / hospital waste incinerator (higher contribution of 1,2,3,4,6,7,8 HpCDF and OCDF). The impact of coal fired power generating plants appears to be dominating over other emissions sources.

- At location S, the congener profile reflects a combined effect of coal fired power generating facilities (higher contribution of 1,2,3,4,6,7,8 HpCDD and OCDD compared to rest of dioxin congeners) and medical / hospital waste incinerator (high contribution of 1,2,3,4,6,7,8 HpCDF and OCDF). The impact of medical / hospital waste incinerators appears to be dominating over other sources. There has been a higher than normal contribution of 1,2,3,7,8 PeCDF and 1,2,3,4,7,8,9 HpCDF and its reasons could not be understood.

- The congener profile in samples of location W is though similar in congener profile to that of location CE but the contribution of tetra, penta and hexa CDDs are relatively higher. The location is farther from thermal power generating facilities as well as medical / hospital waste incinerator but there are numerous combustion sources in nearby industrial units/clusters.

- The contribution of 1,2,3,4,6,7,8 HpCDF and OCDF was relatively higher with respect to the contribution of 1,2,3,4,6,7,8 HpCDD and OCDD in PCDD/F samples of location NE, which is characteristic to the combustion of mixed industrial waste and the same may be attributed to the small scale industrial units located in the area suspected to be burning high calorific waste material for operation of boilers and other equipments.

- In the congener profile of samples from monitoring location N, the contribution of OCDD was > 18% and that of OCDF at > 12%. The penta, hexa and hepta CDDs and CDFs were found contributing about 4 to 6% and the tetra CDD and CDF contributed less than 2%. The observed profile could not be conclusively attributed to any specific source category however there are possibilities of contribution from refuse barrel burning, copper electrical wire manufacturing.

It is summarized from the above observations that the contribution of gasoline driven automobiles can be attributed to all monitoring locations, however the impact of thermal power plants and medical / hospital waste incinerator is dominant on locations nearby these sources. The locations farther from these major known sources have impact of local industrial units combusting various fuels and probably mixed industrial wastes.

Acknowledgements
The authors are thankful to the concerned officials of Air Laboratory, CPCB, Headquarters. for respirable suspended particulate matter sample collection from ambient air on glass fiber filter papers at monitoring locations of National Ambient Air Monitoring Programme. The extensive contribution of officials of National Reference Trace Organics Laboratory during processing of the samples is also thankfully acknowledged.

References
1. Srogi K. *Environ Chem Lett* 2008; 6:1-28.
2. Rappe, C. *Pure & Appl. Chem.* 1996; 68:1781-1789.
3. USEPA Report EPA/600/P-03/002f, 2006.
4. Cleverly, D.; Schaum, J.; Schweer, G.; Becker, J.; Winters, D. *Organohalogen Compounds* 1997; 32:430-435.
5. Lorber, M.; Braverman, C.; Gehring, P; Winters, D; Sovocool, W. *Chemosphere* 1998; 37:2173-2197.
6. Hagenmaier, H.; Lindig, C.; She, J. *Chemosphere* 1994; 29: 2163-2174.